

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

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PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

14.04.2005

Applicant's or agent's file reference
SMC 60559/WO

IMPORTANT NOTIFICATION

International application No.
PCT/GB 03/04928

International filing date (day/month/year)
13.11.2003

Priority date (day/month/year)
15.11.2002

Applicant
AVECIA LIMITED

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

| DATE ENTERED INTO | DATE | INITIALS |
|-------------------|---------|----------|
| FILE | 15/4/05 | CS |
| TO BE VERIFIED | | |
| ENTRY VERIFIED BY | | |
| ATTORNEY | | |

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Article 36 and Rule 70)



| | | |
|--|--|---|
| Applicant's or agent's file reference SMC 60559/WO | FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416) | |
| International application No. PCT/GB 03/04928 | International filing date (day/month/year) 13.11.2003 | Priority date (day/month/year) 15.11.2002 |
| International Patent Classification (IPC) or both national classification and IPC C09B35/362 | | |
| Applicant AVECIA LIMITED | | |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

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|---|--|
| Date of submission of the demand 07.04.2004 | Date of completion of this report 14.04.2005 |
| Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016 | Authorized Officer Ginoux, C Telephone No. +31 70 340-2839  |

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/GB 03/04928**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-34 as originally filed

Claims, Numbers

1-21 received on 04.02.2005 with letter of 01.02.2005

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

| | | |
|-------------------------------|-------------|---------------------|
| Novelty (N) | Yes: Claims | 1-5,7,8,11-13,15-21 |
| | No: Claims | 6,9,10,14 |
| Inventive step (IS) | Yes: Claims | 1-5,7,8,11,13,15-21 |
| | No: Claims | 6,9,10,14 |
| Industrial applicability (IA) | Yes: Claims | 1-21 |
| | No: Claims | |

2. Citations and explanations

see separate sheet

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Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following documents:

- D1: WO 01/62854 A (SHIMIZU WATARU ;MITSUBISHI CHEM CORP (JP)) 30 August 2001 (2001-08-30)
- D2: DE 268 488 C (FARBENFABRIKEN VORM. FRIEDR. BAYER & CO)
- D3: DE 87 973 C (LEOPOLD CASSELLA & CO.) 14 July 1896 (1896-07-14)
- D4: DE 894 423 C (CASSELLA FARBWERKE MAINKUR AG) 26 October 1953 (1953-10-26)
- D5: GB-A-1 569 259 (ICI LTD) 11 June 1980 (1980-06-11)
- D6: EP-A-0 051 785 (BAYER AG) 19 May 1982 (1982-05-19)
- D7: GB 741 578 A (CIBA LTD) 7 December 1955 (1955-12-07)

Novelty

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 6,9,10 and 14 is not new in the sense of Article 33(2) PCT.

The documents D2-D5 disclose (see the relevant parts cited in the International Search Report) tris-azo compounds which are not in the form of a metal chelate and which correspond to formula (1) of claim 6 and to the more preferred embodiments of claims 9, and/or 10 and/or to the definition of claim 14.

Documents D1, D6 and D7 disclose metal chelates and are therefore not relevant any more against novelty.

Inventive step

In the technical field of dyes for ink-jet printing the document D1 is regarded as being the closest prior art to the subject-matter of claim 1. D1 discloses trisazo compounds which are chelated with a metal. As demonstrated by the applicant by comparative data, the use of the compounds of formula (1) in a process for printing images on various substrates results in superior properties than the use of corresponding metal chelates. It is also claimed that the

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International application No. PCT/GB 03/04928

compounds are cost effective to produce and more environmentally friendly. The problem to be solved can be seen in the provision of a process for printing an image on a substrate with azo compounds resulting in improved properties. The solution proposed in present claim 1 appears to be inventive since it would not be obvious for a skilled person with the knowledge of D1 to use non-metallised tris-azo dyes in a printing process in order to achieve better printing results.

Also the combination of the teaching of D1 with that of D2-D5, which disclose non-metallised tris-azo dyes would not appear obvious for a skilled person since these documents belong to different technical fields.

Consequently the subject-matter of present claim 1 can be considered as involving an inventive step (Article 33(3) PCT).

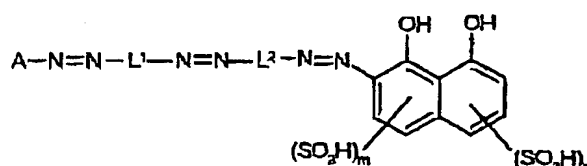
The same reasoning applies, *mutatis mutandis*, to the subject-matter of the corresponding independent claims 15,19,20 and 21 which therefore are also considered inventive.

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Claims

1. A process for printing an image on a substrate comprising applying thereto a composition comprising a liquid medium and a tris-azo compound of Formula (1) or salt thereof;



Formula (1)

wherein:

A is an optionally substituted alkenyl, homocyclic or heterocyclic group;
L¹ and L² are each independently optionally substituted aryl or heteroaryl; and
m and n are each independently 0 or 1 such that m+n is 1 or 2;

wherein:

- (i) the compound of Formula (1) is not in the form of a metal chelate; and
- (ii) at least one of L¹ and L² carries at least one substituent selected from sulpho, carboxy, C₁₋₄-alkoxy and C₁₋₄-alkoxy-OH.

2. A process according to claim 1 wherein the composition is applied to the substrate by means of an ink jet printer.

3. A process according to any one of the preceding claims wherein the image is text, a picture, a photorealistic image or a combination thereof.

4. A process according to any one of the preceding claims wherein the substrate is paper, plastic, metal or glass.

5. A process according to any one of the preceding claims wherein:

A is optionally substituted pyridyl, furyl, thienyl, thiazolyl, isothiazolyl, imidazolyl, benzimidazolyl, pyrazinyl, pyrimidyl, quinolyl, isoquinolyl, benzofuryl, benzothienyl, pyrazolyl, indolyl, purinyl, isoxazolyl, oxazolyl, thiadiazolyl, furazanyl, pyridonyl, pyrazolonyl, piperidinyl, piperazinyl, pyrrolidinyl, morpholinyl, tetrahydrofuranyl, tetrahydrothiophenyl or tetrahydropyranyl;

L¹ phenyl or naphthyl optionally carrying a substituent selected from sulpho and carboxy;

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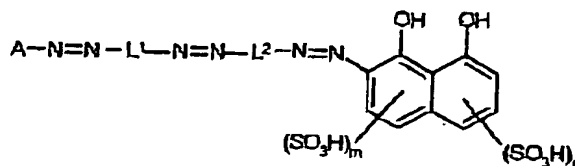
L^2 is phenyl or naphthyl carrying at least one substituent selected from sulpho, carboxy C_{1-4} -alkoxy and C_{1-4} -alkoxy-OH; and

m and n are each independently 0 or 1 such that m+n is 1 or 2;

wherein said optional substituents are selected from OH; SO_3H ; CN; carbonamido;

5 PO_3H_2 ; CO_2H ; NO_2 ; NH_2 ; C_{1-4} -alkyl optionally carrying a sulpho, carboxy, phosphato, C_{1-4} -alkoxy, amino or hydroxy group; C_{1-4} -alkoxy optionally carrying a sulpho, carboxy, phosphato, C_{1-4} -alkoxy, C_{1-4} -alkyl, amino or hydroxy group; phenyl or phenyl carrying from 1 to 3 substituents selected from sulpho, carboxy, phosphato, C_{1-4} -alkoxy, amino, hydroxy and N carrying one or two C_{1-4} -alkyl groups optionally carrying a sulpho, carboxy, phosphato, C_{1-4} -alkoxy, amino or hydroxy group; N carrying one or two C_{1-4} -alkyl groups optionally carrying a sulpho, carboxy, phosphato, C_{1-4} -alkoxy, amino or hydroxy group; and C_{1-4} -acylamino.

6. A tris-azo compound of Formula (1) or salt thereof:



Formula (1)

wherein:

A is an optionally substituted alkenyl, homocyclic or heterocyclic group;

L^1 and L^2 are each independently optionally substituted aryl or heteroaryl;

m and n are each independently 0 or 1 such that m+n is 1 or 2; and

with the provisos that:

(i) the compound of Formula (1) is not in the form of a metal chelate;

(ii) L^1 and L^2 are each independently optionally substituted phenylene or naphthylene;

(iii) optional substituents present on L^1 and L^2 are selected from OH, SO_3H , CN, carbonamido, PO_3H_2 , CO_2H , NO_2 , NH_2 , optionally substituted alkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted amine and optionally substituted acylamine;

(iv) at least one of L^1 and L^2 carries at least one substituent selected from sulpho, carboxy, C_{1-4} -alkoxy and C_{1-4} -alkoxy-OH; and

(v) when L^1 carries a methoxy group A is not 1,3-diaminophenyl.

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7. A compound according to claim 6 wherein A is optionally substituted pyridyl, furyl, thienyl, thiazolyl, isothiazolyl, imidazolyl, benzimidazolyl, pyrazinyl, pyrimidyl, quinolyl, isoquinolyl, benzofuryl, benzothienyl, pyrazolyl, indolyl, purinyl, isoxazolyl, oxazolyl, thiadiazolyl, furazanyl, pyridonyl, pyrazolonyl, piperidinyl, piperazinyl, pyrrolidinyl, morpholinyl, tetrahydrofuranyl, tetrahydrothiophenyl or tetrahydropyranyl.

8. A compound according to claim 6 wherein A is optionally substituted pyridonyl.

9. A compound according to any one of claims 6 to 8 wherein L^1 is phenyl or naphthyl optionally carrying a substituent selected from sulpho and carboxy.

10. A compound according to any one of claims 6 to 9 wherein L^2 is phenyl or naphthyl carrying at least one substituent selected from sulpho, carboxy, C_{1-4} -alkoxy and C_{1-4} -alkoxy-OH.

11. A compound according to any one of claims 6 to 10 wherein L^2 is phenyl carrying two C_{1-4} -alkoxy-OH substituents.

12. A compound according to claim 6 wherein:

- 20 A is optionally substituted pyridyl, furyl, thienyl, thiazolyl, isothiazolyl, imidazolyl, benzimidazolyl, pyrazinyl, pyrimidyl, quinolyl, isoquinolyl, benzofuryl, benzothienyl, pyrazolyl, indolyl, purinyl, isoxazolyl, oxazolyl, thiadiazolyl, furazanyl, pyridonyl, pyrazolonyl, piperidinyl, piperazinyl, pyrrolidinyl, morpholinyl, tetrahydrofuranyl, tetrahydrothiophenyl or tetrahydropyranyl;
- 25 L^1 phenyl or naphthyl optionally carrying a substituent selected from sulpho and carboxy;
- L^2 is phenyl or naphthyl carrying at least one substituent selected from sulpho, carboxy, C_{1-4} -alkoxy and C_{1-4} -alkoxy-OH; and
- 30 m and n are each independently 0 or 1 such that $m+n$ is 1 or 2; wherein said optional substituents are selected from OH; SO_3H ; CN; carbonamido; PO_3H_2 ; CO_2H ; NO_2 ; NH_2 ; C_{1-4} -alkyl optionally carrying a sulpho, carboxy, phosphato, C_{1-4} -alkoxy, amino or hydroxy group; C_{1-4} -alkoxy optionally carrying a sulpho, carboxy, phosphato, C_{1-4} -alkoxy, C_{1-4} -alkyl, amino or hydroxy group; phenyl or naphthyl carrying from 1 to 3 substituents selected from sulpho, carboxy, phosphato, C_{1-4} -alkoxy, amino, hydroxy and N carrying one or two C_{1-4} -alkyl groups optionally carrying a sulpho, carboxy, phosphato, C_{1-4} -alkoxy, amino or hydroxy group; N carrying one or two C_{1-4} -alkyl groups optionally carrying a sulpho, carboxy, phosphato, C_{1-4} -alkoxy, amino or hydroxy group; and C_{1-4} -acylamino.

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13. A tri-azo compound of Formula (1), as shown in claim 6, or a salt thereof, wherein:

A is pyridonyl carrying at least one substituent selected from carbonamido and C₁₋₄ alkyl;

5 L¹ is phenyl carrying at least one sulpho substituent;

L² is phenyl carrying at least one substituent selected from sulpho, carboxy, C₁₋₄-alkoxy and C₁₋₄-alkoxy-OH; and

m and n are both 1;

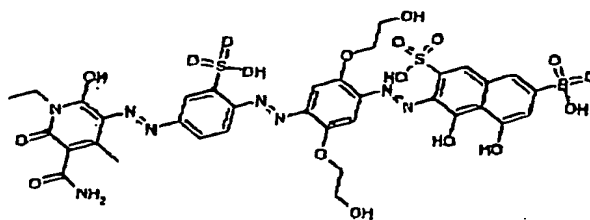
provided that the compound of Formula (1) is not in the form of a metal chelate.

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14. A compound as defined in any one of the Examples described herein.

15. A composition comprising a compound of Formula (1) or salt thereof as defined in claim 1 and a low melting point solid or a liquid medium comprising water and an organic solvent, wherein the compound of Formula (1) is not Formula (3) or a salt thereof.

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Formula (3).

20 16. A composition according to claim 15 wherein the compound of Formula (1) is as defined in any one of claims 6 to 14.

17. A composition according to claim 15 or 16 which has a concentration of less than 500 parts per million of halide ions, wherein parts refer to parts by weight relative to the total weight of the composition.

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18. A composition according to any one of claims 15 to 17 which has less than 50 parts per million of divalent and trivalent metals, wherein parts refer to parts by weight relative to the total weight of the composition.

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19. A paper, an overhead projector slide or a textile material printed with a composition according to claim 15, 16, 17 or 18 or a compound according to any one of claims 6 to 14 or by means of a process according to any one of claims 1 to 5.

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20. An ink jet printer cartridge, optionally refillable, comprising one or more chambers and a composition, wherein the composition is present in at least one of the chambers and the composition is as defined in any one of claims 15 to 18.

5 21. Use of a compound of Formula (1), as defined in claim 1, in ink jet printing.

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